Procedure for Fitting Non-Newtonian Viscosity Data

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Steady state non-Newtonian viscosity data typically vary over several decades or more in viscosity and shear rate (or shear stress) for many concentrated polymer solutions and polymer melts. Rheological models are fitted to such data as a basis for testing theories for momentum transfer, understanding molecular characteristics of the system described by such theories, and interpretation and correlation of the macroscopic properties associated with mass, heat and momentum transfer in non-Newtonian systems. Several graphical procedures have been developed but these are applicable only to specific models (*1* to *5*). Numerical procedures have been used (*6*, *7*) but no consideration has been given to how the sampling of the data and the fitting procedure affect the fit.

The principal considerations in data fitting are (*8*) the choice of approximating function, how the data are sampled, the error term, and the criteria for defining how good the fit is. Since the approximating function is prespecified, only the latter three are open to choice. The discussion will be confined to pseudoplastic behavior, which is the dominant form of non-Newtonian viscous behavior manifested. In this case the major variation in viscosity is crowded into a relatively small region at low shear rates. In polymer solutions a limiting viscosity is approached at high shear rates. The application of the procedure to other forms of non-Newtonian behavior follows naturally.

DATA SAMPLING

The data sampling procedure may be specified at either of two times. The best time, of course, is during the planning of the experimental design. However, hindsight or convenience may dictate another choice after the experimental data have been gathered. In particular, data may be graphically smoothed and then sampled for subsequent fitting.

Assuming for the moment the latter case, the most common procedure is to sample at equal increments in the independent variable, such as, the shear rate. It is clear that this will place proportionately more data points at high shear rates in the region where the viscosity is changing slowly. Information in the region of most rapidly changing viscosity, at low shear rates, may be lost because of insufficient sampling. This can be corrected by decreasing the sampling interval and, in the limit, the sampling density will be infinite and information is completely preserved in the sampled data. Suppose, however, a fitting procedure using redundant information such as least squares is used. The proportionate number of data points in the region of slowly changing viscosity is far in excess of those in the region of rapidly changing viscosity. Consequently, small errors at high shear rates are given more weight than larger errors at low shear rates. The fit of the data is better at high shear rates at the expense of the data at low shear rates.

It is evident that the sampling procedure must satisfy three requirements. The sampling interval must be small enough to preserve the desired information. The sampling procedure should weight the data according to how rapidly the viscosity changes with shear rate. Finally, the data should be sampled at an economical rate so that they are not excessive in number.

Information may uniformly be preserved in the data sample by sampling at an interval such that the viscosity changes by no more than a prespecified fractional amount. By using this criteria the interval between the n and $(n + 1)$ data points, where the shear rate increases with increasing n, is defined by

$$\frac{\eta_{n+1}}{\eta_n} \geq \psi \tag{1}$$

The maximum fractional change in the viscosity over the sampling interval is $(1 - \psi)$. Since the viscosity decreases monotonically $\psi < 1$. The sampling interval decreases with increase in ψ.

Normally, between the limiting viscosities at high and low shear rates, there is an extended power law region. The slope of this region is $(-\alpha)$ and

$$\frac{\Delta \log \eta}{\Delta \log |\dot{\gamma}|} = -\alpha = -(1 - n) \tag{2}$$

where n is the flow behavior index. The viscosity-shear rate data between any two points in this region is related by

$$\frac{\eta_{n+1}}{\eta_n} = \left(\frac{|\dot{\gamma}|_{n+1}}{|\dot{\gamma}|_n}\right)^{-\alpha} \tag{3}$$

The sampling interval is defined by

$$\Delta|\dot{\gamma}|_n = |\dot{\gamma}|_{n+1} - |\dot{\gamma}|_n \tag{4}$$

The nth sample interval in the power law region, upon combination of Equations (1), (3), and (4), is defined as

$$\Delta|\dot{\gamma}|_n = |\dot{\gamma}|_n \, (\psi^{-1/\alpha} - 1) \tag{5}$$

For a given viscosity curve and choice of ψ, $\psi^{-1/\alpha}$ is constant and can be replaced by

$$\beta = \frac{1}{\alpha} \log (1/\psi) \tag{6}$$

From Equations (1) and (3)

$$\beta = \log (|\dot{\gamma}|_{n+1}) - \log (|\dot{\gamma}|_n) \tag{7}$$

and β clearly defines a logarithmic sampling interval constituting equal increments in the shear rate on logarithmic coordinates.

As an example, consider the data given by Philippoff, et al. (*9*) for a 1% solution of nitrocellulose in n-butyl acetate. This system is highly non-Newtonian and the viscosity varies by a factor of 100,000 between its limiting values. The value of ψ chosen was 0.5 and $\alpha = 0.87$. From Equation (6), $\beta = 0.33$. The data should be sampled at one-third decade intervals in the shear rate. When the data are only slightly non-Newtonian, ψ should

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be increased, approaching 1.

The sampling procedure specified by Equations (6) and (7) clearly satisfies the three stated objectives. Sample interval size is adjusted by ψ which defines the level of information preservation. The sampling rate is directly associated with the rate at which the viscosity decreases by the quantity α. Finally, the procedure is economic, requiring a minimum of data points as defined by the previous two considerations.

For the case where the experimental design is being planned, α is assumed for the viscosity curve not yet determined. Usually a fair estimate of α can be made from past experience.

Meter (*6*) almost used a logarithmic sampling interval (in shear stress) for fitting a modified Reiner-Philippoff model to select data. The sampling procedure most generally used in practice, however, is an intuitive one.

ERROR TERM

The error term may be formed in several ways. Because a small relative error at low shear rates may represent a large absolute error in relation to the corresponding relative error at high shear rates, the error should not depend upon the absolute magnitude of the viscosity. This avoids overshadowing small but significant absolute errors at high shear rates by large but less significant absolute errors at lower shear rates when using a fitting procedure such as least squares. In most engineering studies the relative error is the more significant figure. In addition, positive and negative deviations should be treated alike.

Four forms of the error term can be constructed. These are listed as follows:

$$\epsilon_{1i} = (f_i - y_i) \tag{8a}$$

$$\epsilon_{2i} = |f_i - y_i| \tag{8b}$$

$$\epsilon_{3i} = \log f_i - \log y_i \tag{8c}$$

$$\epsilon_{4i} = (f_i - y_i)/f_i \tag{8d}$$

The error terms in Equation (8*a*) and (8*b*), while commonly used (*6, 7*), are not satisfactory because they depend upon the magnitude of the viscosity. The error term in Equation (8*c*) treats positive and negative deviation differently.

Only Equation (8*d*) is satisfactory. This form of the error term should be used where the viscosity varies by roughly an order of magnitude or more. It has been used extensively and successfully for fitting varied non-Newtonian data to rheological models (*10*).

FITTING CRITERIA

The least squares or the Chebyshev criteria may be used as a basis for establishing how well the data are fitted by an approximating function. The former is well known and widely used and leads to the minimization of the sum of the squared error. The latter leads to the minimization of the maximum error. It is also called the *minimax* principle (*8*) and has the valuable property of establishing bounds on the maximum error. These two criteria are, formally:

least squares:

$$\frac{\partial}{\partial \alpha_j}\left(\sum_{i=1}^{N} \epsilon_i^2\right) = 0 \quad (j = 1, \ldots M) \tag{9a}$$

Chebyshev:

$$\frac{\partial}{\partial \alpha_j}|\epsilon_i\,(\max)| = 0 \quad (j = 1, \ldots M) \tag{9b}$$

where α_j is the jth parameter in a set of M parameters. Numerically the Chebyshev criteria is an iterative extension of the least squares procedure. The error terms of each succeeding iteration are weighted by the corresponding error terms of the immediately preceding iteration raised to a power increasing with the number of iterations.

The two criteria were applied to fitting the solution data of Philippoff, et al. to select rheological models. The least squares procedure resulted in a fit of the data that did not favor any portion of the viscosity curve. The fitted curve uniformly described the data over the full range of shear rates considered within the quantitative limitations of the models to do so. On the other hand the Chebyshev criteria resulted in a solution for the undetermined model parameters that oscillated unstably about the least squares solution. Rather than minimize the maximum error the maximum error actually increased with each iteration. Though these observations are based on only one set of data this set is representative of many non-Newtonian systems and it appears that the Chebyshev criteria are not applicable to fitting non-Newtonian viscosity data.

CONCLUSION

The collective application of the data sampling procedure, the error term and the least squares procedure to fitting non-Newtonian viscosity data assures that, within the limitations of the approximating function, the data are fit equally well at all shear rates (or shear stresses). This procedure has been used to fit numerous viscosity data for diverse non-Newtonian solutions and polymer melts with entirely satisfactory results (*10*). Application of such a procedure establishes the common basis necessary for the comparison and confident exchange of parametric data so important in engineering studies.

NOTATION

f_i = experimental value of dependent variable
y_i = fitted value of dependent variable
n = flow behavior index

Greek Letters

α = Equation (2)
α_j = parameter value
β = Equation (6)
$\dot{\gamma}$ = shear rate
ϵ = error term, Equation (8)
η = viscosity
ψ = Equation (1)

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